

# MEASUREMENT OF ELECTRICAL PROPERTIES OF UNDOPED DIAMOND FILMS BETWEEN ROOM TEMPERATURE AND 1000 °C

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## ABSTRACT

The high temperature electrical resistivity, measured between room temperature and 1000 °C, of undoped diamond films has been shown to be a very accurate determination of the quality of these films (1). The diamond films currently being grown - just about all - have the same resistivity at room temperature of around  $10^1$  -  $10^6$  Ω-cm, which has been shown to be the apparatus-limited value (2), but at higher temperatures the resistivities can differ by up to five orders of magnitude. The best films now have resistivities about two orders of magnitude greater than that for natural type IIa diamond, and are significantly better than the resistivities obtained on the best films only a few years ago. The cooling curves, from 1000 °C back to room temperature, all have a lower resistivity compared to the resistivity of the heating curves. This is believed to be due to some surface conduction as a result of the formation of non-diamond carbon on the surface due to some graphitization. This observed change in resistivity is just one of several pitfalls that are encountered during electrical resistivity measurements at high temperatures.

*almost all of*

## INTRODUCTION

The quality of diamond films synthesized by CVD, arcjet and combustion flame has improved greatly over the past few years. This improved quality has been observed optically (very clear diamond films) and in the Raman spectra that are now nearly the same or even identical to that for natural diamond (without the additional peaks indicative of non-diamond phases such as graphite, amorphous carbon, etc.). Also, the thermal conductivity and electrical resistivity of diamond films have approached, equaled and in some cases exceeded that for the best natural type IIa diamonds (1,3,4). However, there is no quick and accurate method of determining the quality of a diamond film. The Raman spectrum is sensitive to  $sp^2$  bonded carbon (non-diamond carbon) but not other defects while the room temperature thermal conductivity, which is not easy to measure accurately, is determined by impurity, grain boundary, and phonon-phonon scattering. So a high purity small grain size film could have a very low thermal conductivity.

The electrical conductivity is very sensitive to all impurities and defects involved in the conduction process but it has been shown by Vandersande and Zoltan (2) that at room temperature the lowest conductivities, of natural insulating type IIa diamond and the best diamond film samples, are at the limits of the measuring apparatus (i.e. resistivity values higher than about  $10^{16}$  Q-cm cannot be measured). The real resistivity values of natural diamond and the best films are thus considerably higher than this "apparatus-limited" value. Diamond films with these high resistivity values can now routinely be grown, compared to typical room temperature resistivity values of  $10^8$  to  $10^{15}$  Q-cm only a few years ago. Also, the best films have resistivities greater than that for natural type IIa diamond over the whole temperature range. Several examples will be shown and discussed. In addition, room temperature resistivity measurements depend on the condition of the surface of the film (2,3) making interpretation of the data very difficult. However, the conductivity of diamond increases with increasing temperature making measurements easier at higher temperatures. As a result, high temperature (up to 1000 °C) electrical conductivity data can be used as one of the main determinants of the quality of diamond films as has been shown recently (1).

Electrical resistivity measurements of insulators at high temperatures are not simple, and especially with diamond, there are a few pitfalls that are specific to diamond. Several of these pitfalls will be discussed below and precautions and techniques on how to avoid them will be given.

## EXPERIMENTAL DETAILS

The experimental approach utilized for the room and high temperature resistivity measurements has been described elsewhere (2). Briefly, the resistivity is measured perpendicularly through the sample, which is placed in an alumina holder. The top and bottom electrodes are iridium foils, with the sample resting on one foil and the second foil pressed against the sample by means of a niobium rod (with a small weight placed on it). Iridium was used since it does not form a carbide with the diamond at the temperatures used in the measurements. This type of electrode configuration does result in ohmic behavior in the range of voltages used (+100 V to -100 V) (1,2). A Keithley 617 electrometer (high output impedance) was used for the measurements. Originally a guard ring was used on the larger samples but it was found that identical results were obtained without a guard ring on the heating curve up to 1200 °C as long as the data were taken within a period of several hours. This result made it possible to dispense with the guard ring, which is an advantage since it is very difficult to use on small and irregularly shaped samples. The vacuum level in the test station was 10-S- 10-6 Torr.

The diamond films were supplied by several different companies. Astex supplied three free standing films (white, grey, and black) grown using their high purity and

standard techniques respectively. The films were all 380  $\mu\text{m}$  thick. Crystallume supplied two samples: the first (6  $\mu\text{m}$  thick on Si) was grown a few years ago using their then standard process, while the second one was a free-standing clear, colorless film 300  $\mu\text{m}$  thick grown recently by microwave plasma CVD using their high purity technique. The Norton sample was a free-standing greyish film 1.1 mm thick grown by their arcjet process. The Lockheed sample was a clear free-standing film 80  $\mu\text{m}$  thick grown using their combustion flame technique. Finally, the Raytheon sample was a clear free-standing film 660  $\mu\text{m}$  thick grown using their microwave plasma CVD technique. All the samples except the first Crystallume sample were polished (at least on one side) and the free-standing films were cleaned by us before measurement.

## EXPERIMENTAL RESULTS AND DISCUSSION

The electrical conductivity versus inverse temperature between room temperature and 1000-1200  $^{\circ}\text{C}$  for the two Crystallume, the Norton and the Raytheon diamond films are shown in figure 1, for the Lockheed film in figure 2, and for the Astex films in figure 3. The conductivity of natural type IIa diamond is shown for comparison. The conductivity of this natural diamond is approximately constant in the  $10^{-16}$  to  $10^{-15} \Omega^{-1}\text{cm}^{-1}$  range between room temperature and 200  $^{\circ}\text{C}$ . This is the "apparatus-limited" value, which is the lowest conductivity the apparatus will measure and represents the leakage currents around the sample through the holder (2.). All samples, except the first Crystallume sample and the grey and black Astex samples, also show this "apparatus-limited" value with white Astex, the second Crystallume, the Lockheed, and the Raytheon samples having this value up to the 200-300  $^{\circ}\text{C}$  range while the Norton sample has it up to about 130  $^{\circ}\text{C}$ . These five samples thus all have resistivities that would be expected to be greater than  $10^{15} \Omega\text{-cm}$  at room temperature. This is a great improvement over samples grown only a few years ago (as a comparison with the first Crystallume sample clearly shows). The fact that five of the films have lower conductivities than that for natural type IIa diamond over the whole temperature range, indicates that these polycrystalline films have less defects (that are involved in the conduction process) and are thus purer than a good quality single crystal diamond. The Norton sample was not made with purity in mind but was made for thickness. The slightly higher conductivity for this sample in the 150-1000  $^{\circ}\text{C}$  range shows that even though five of the samples all have the same "apparatus-limited" room temperature conductivity, the high temperature conductivities can differ by 2 to 3 orders of magnitude. Similarly, the grey and black Astex samples and the first Crystallume sample have a room temperature conductivity of about  $10^{-14} \Omega^{-1}\text{cm}^{-1}$  to  $10^{-13} \Omega^{-1}\text{cm}^{-1}$ , which is right at the limit of the apparatus, but have a very noticeably higher conductivity at higher temperatures. These results thus clearly indicate that the room temperature resistivity measurement by itself is not sufficient to determine the quality of a diamond film. These two Astex samples have a conductivity that only equals that for natural diamond at the very highest temperatures. This high conductivity is believed to be

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due to non-diamond carbon at the grain boundaries providing a conduction path for the charge carriers. Also, the Raman spectra of most the high resistivity samples were all nearly equal to if not identical to that for natural diamond (with no additional peaks). Hence, the Raman spectra alone cannot indicate the comparative quality of the films as high temperature resistivity data can. The activation energies of the five low conductivity films and of the natural IIa diamond are all in the 1.50-1.60 eV range. This energy is believed to be associated with the isolated substitutional nitrogen (5).

The cooling curves for the five samples are not shown in figures 1, 2, and 3 but cooling curves are shown for the Norton sample in figure 4. The cooling curves for the other samples were reasonably similar and were omitted for clarity. There are some differences in cooling curves which are believed to be due to different diamond crystallographic orientations graphitizing at different rates. This orientation dependent graphitization is currently under investigation and will be reported at a later date. The higher conductivity on the cooling curve is due to surface leakage paths that result from surface graphitization. This non-diamond carbon surface contaminant can be removed in concentrated acids, restoring the original low conductivities. Reheating the samples then resulted in data falling exactly on the original curves. There is evidence that some graphitization (e.g. a monolayer) starts as low as 450°C (6) and that CO desorbs from the surface as low as 250°C, resulting in some surface reconstruction (7). Other contaminants as well as non-diamond carbon will also result in higher conductivities. This can clearly be seen in figure 4 where the conductivity for the film in the as-received condition (not cleaned after polishing and cutting) has a high conductivity (about  $10^{-11} \Omega^{-1} \text{cm}^{-1}$ ) while after an acid clean the conductivity drops to the "apparatus-limited" value. The three Astex samples had room temperature conductivity values of  $10^{-8} \Omega^{-1} \text{cm}^{-1}$  to  $10^{-10} \Omega^{-1} \text{cm}^{-1}$  before cleaning which dropped to the values shown in figure 3 after the acid clean. Based on this result it is suspected that numerous room temperature electrical resistivity results, reported in the literature, probably were measured on "dirty" samples so were not indicative of the true resistivity of the samples. As a point of interest, a few years ago the samples we measured only had room temperature conductivities in the  $10^{-14}$  to  $10^{-10} \Omega^{-1} \text{cm}^{-1}$  range (2) and the conductivities only approached that of natural diamond at the highest temperatures. The quality of the current diamond films is thus significantly better than those synthesized only a few years ago.

Hydrogen adsorbed to the diamond film surface, as a result of the synthesis in a hydrogen-hydrocarbon atmosphere, also results in a higher conductivity with a different temperature behaviour, if it is not removed. An as-fabricated microwave plasma CVD diamond film grown at North Carolina State University had a conductivity that was approximately constant at  $10^{-10} \Omega^{-1} \text{cm}^{-1}$  between room temperature and 300°C and then followed the conductivity for the natural diamond up to 1000°C. On the cooling curve the conductivity came back to  $10^{-5} \Omega^{-1} \text{cm}^{-1}$  at room temperature (3). The lower conductivity is thus the real conductivity of the film. The adsorbed hydrogen, which had probably

come off by 300 °C, has a pronounced effect and underestimates the resistivity of the diamond film if only room temperature values are measured.

The effect of surface finish on the measured conductivity was found to have only a slight effect as is shown in figure 2 for the Lockheed sample. This combustion flame grown film had a polished side (where the substrate was removed) and a rough side (growth side). The conductivity of the sample with the polished side up is as low as that found for the Crystallume and Raytheon samples (see figure 1), but is about one order of magnitude higher than that found with the rough side up. This lower conductivity is believed to be due to the top iridium electrode foil, which is pressed against the sample, only making contact with the diamond crystallite peaks and top facets, so not making uniform contact over the full area of the foil. In the case of the polished surface uniform contact is very likely made over the whole foil area and the correct conductivity measured. This was confirmed by putting a graphite cement contact, of the same size as the top Ir foil, on the polished side and then performing the measurement as usual. The conductivity was found to be the same as before as shown in figure 2. Care should thus be taken when measuring rough diamond surfaces. The advantage of using press contacts, rather than bonded contacts, is that the diamond film is in no way affected so can be used for other tests or measurements.

## SUMMARY

The electrical conductivity of several diamond films has been measured between room temperature and 1000 °C. Even though the room temperature conductivities were all very similar and equal to the "apparatus-limited" value of  $10^{-15}$  to  $10^{-16} \Omega^{-1} \text{cm}^{-1}$ , the higher temperature conductivities differed by up to several orders of magnitude. These results thus indicate that high temperature electrical conductivities (determined by the impurities and defects involved in the conduction process) are very helpful in determining the purity and relative quality of undoped diamond films. It has also been shown that the room temperature electrical conductivity of a diamond film with a "dirty" surface (contaminants, non-carbon diamond, adsorbed hydrogen, etc.) can be up to six orders of magnitude higher than that for a film with a cleaned surface. Also, graphitization takes place as low as around 450 °C, resulting in some surface conduction which results in higher conductivities upon cooling.

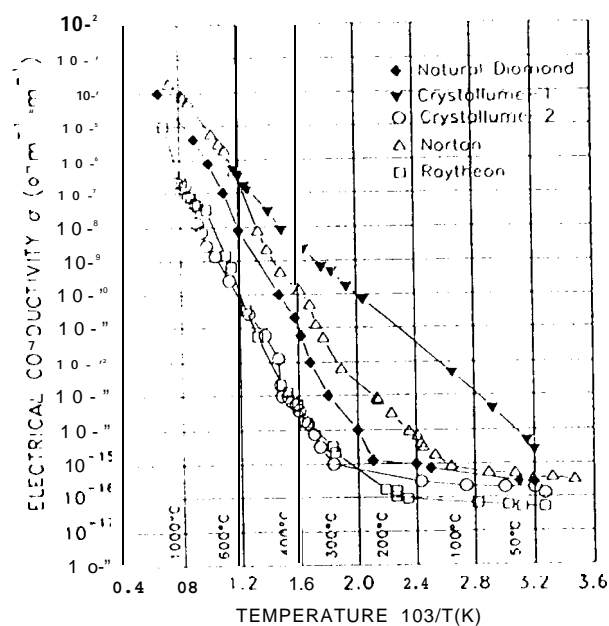
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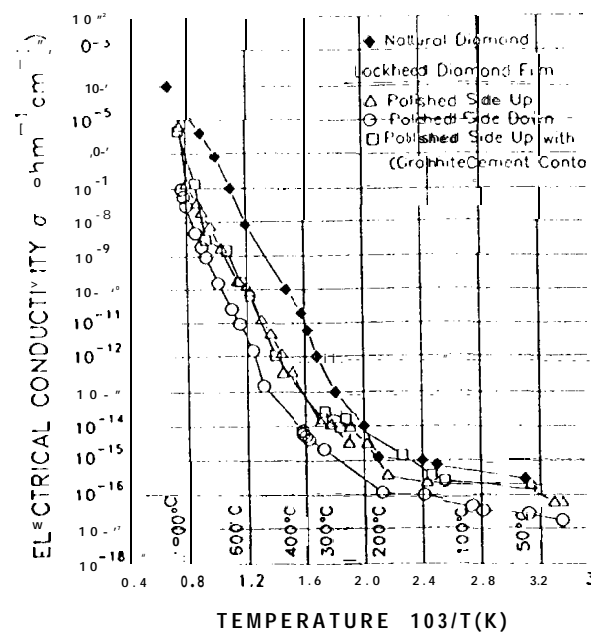
performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration.

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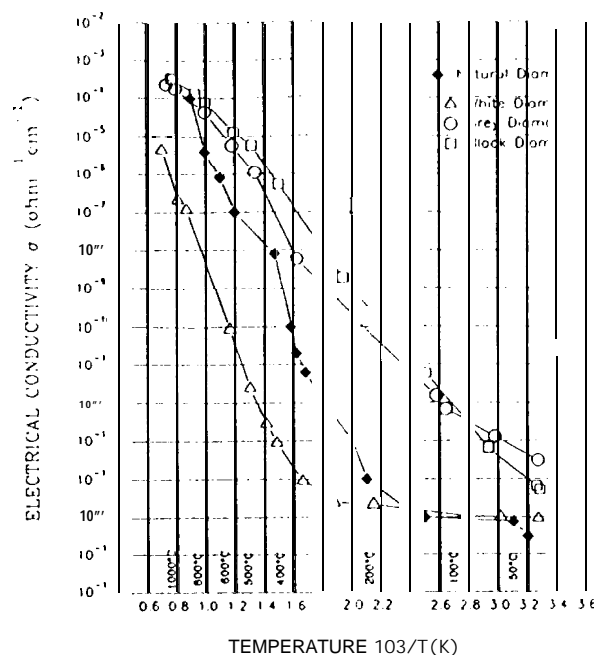
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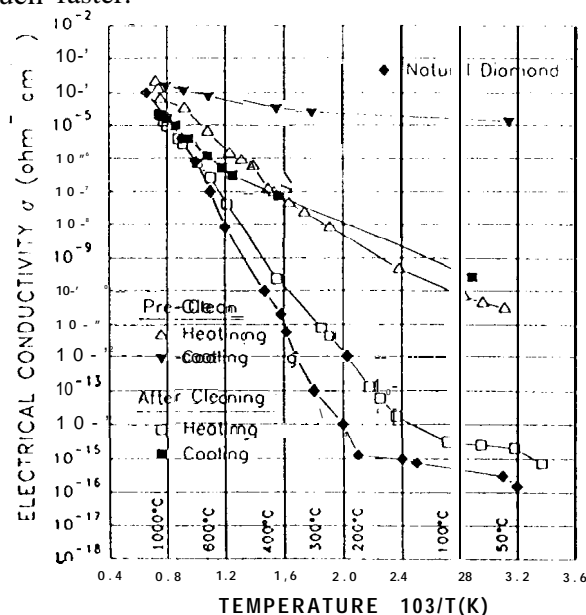
**Figure 1.** Electrical conductivity plotted as a function of reciprocal temperature for four diamond films: Crystallume-1, 6  $\mu\text{m}$  thick on Si, Crystallume-2, free-standing 300  $\mu\text{m}$  thick, Norton, free-standing 1.1 mm thick, and Raytheon, free-standing 660  $\mu\text{m}$  thick. The conductivity of a natural type IIa diamond is also shown. The conductivities at room temperature are the "apparatus-limited" values.



**Figure 2.** Electrical conductivity plotted as a function of reciprocal temperature for a free-standing Lockheed diamond film 80  $\mu\text{m}$  thick. Data for a natural type IIa diamond are also shown. The conductivity was measured with the polished side up, the rough side up, and with a graphite cement contact instead of the usual Ir foil contact.



**Figure 3.** Electrical conductivity plotted as a function of reciprocal temperature for three freestanding Astex diamond films 380  $\mu\text{m}$  thick. Data for a natural type IIa diamond are also shown. The white film was grown using their high purity technique, while the other two were grown much faster.



**Figure 4.** Electrical conductivity plotted as a function of reciprocal temperature for a freestanding Norton diamond film 1.1 mm thick. Data for a natural type IIa diamond are also shown. The conductivity of the film with a "dirty" surface (contaminants and non-diamond carbon) was found to be at least four orders of magnitude greater than that for the film with a cleaned surface.